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POROUS MATERIALS FROM CARBIDES AND BORIDES OF TRANSITION METALS

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POROUS MATERIALS FROM CARBIDES AND BORIDES OF TRANSITION METALS **/85

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Methods of obtaining porous parts from spheroidized powders of carbides and borides are described. The hydraulic characteristics of porous parts were studied, and a dependence was established between the viscosity and the inertial coefficients of porosity resistance.

Many branches of modern technology require materials that retain their strength for a long time at high temperatures and, at the same time, are heat-resistant and have a high resistance to corrosion and to the effect of thermal shocks.

Porous cermet materials made of the carbides and borides of transition metals, having sufficient strength and high permeability, can be used to filter certain liquid metals, incandescent gases, acids, alkalis, and other corrosive media (Bibl.1). An effective method of increasing the power and efficiency of gas turbines and jet engines is to increase the temperature of the working gases, requiring the development of special heat-resistant materials for lining the combustion-chamber walls. In this respect, the use of porous materials of refractory compounds which can be cooled by passing a gaseous or liquid coolant through their pores, is promising (Bibl.2).

Carbides have a high melting point and high hardness, good wear resistance,

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** Numbers in the margin indicate pagination in the original foreign text.

and a satisfactory strength at moderately high temperatures. Borides are the only materials able to withstand high loads in an oxidizing medium in the 1600 - 2200°C temperature range (Bibl.3).

Cermet filters made of powder with spherical particles have high permeability, readily controllable porosity, and are easily regenerated (Bibl.4). In the present work, we investigated methods of obtaining porous materials of spheroidized powders of refractory compounds and studied certain properties of sintered materials. The spherical powders were obtained by the method described previously (Bibl.7).

To create materials with maximal porosity and permeability we used the free-pour method of fabricating porous articles. Sintering of the spheroidized freely poured carbide and boride powders was done in graphite molds and, as a rule, in the presence of activators which most often were cobalt chloride or nickel.

The spheroidized powder was placed in a solution of chloride and dried under constant mixing until complete removal of the solvent. In this case, the cobalt chloride or nickel precipitated on the surface of the powder particles. The dried powder was poured into the molds and sintered at a fusion point of 0.7 - 0.95 T_f of the corresponding material. The sintering time varied from 30 to 240 min. The presence of cobalt chloride (or of nickel) activated the surface of the particles, which made it possible to obtain strong products at a lower sintering temperature. At the same time, despite the relatively large amount of activator added (in some experiments, its content amounted to 3%), the content of cobalt (nickel) in the finished product after sintering was less /86 than 0.1%, which is explained by the high volatility of chlorine compounds with metals.

The specimens for the investigation of the catalytic properties of materials in certain electrochemical processes were prepared by the method of sintering freely poured powders. The sintering temperature had a substantial effect on the porosity of the resultant products and also on their strength characteristics. Figure 1 shows a curve of the porosity as a function of the sintering temperature, for specimens of chromium carbide Cr_3C_2 made by the free-pour

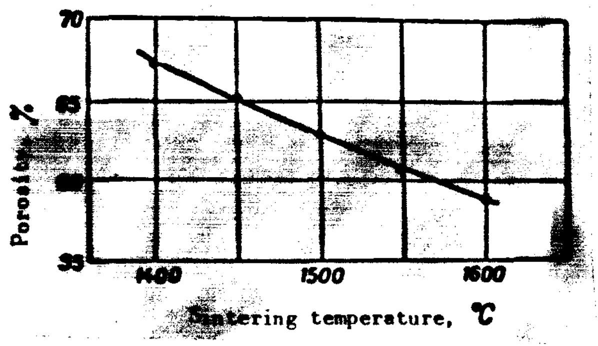

Fig.1 Porosity of Products Produced by Sintering Freely Poured Powder, as a Function of the Sintering Temperature

method from spheroidized particles measuring 100 - 150 μ. Sintering of spheroidized particles of chromium carbide at a temperature below 1400°C resulted in low-strength products. Sintering at temperatures of 1400 - 1600°C produced strong objects, but at a higher temperature we observed partial fusion and closing of the pores. As follows from the curve, the porosity of specimens obtained by the method of sintering freely poured spheroidized powder is high and reaches 68%.

To create materials with a prescribed porosity and permeability and to produce articles of wanted shape, it is advantageous to presinter the spheroidized powders into compacts. We prepared compacts of porous materials both from spheroidized powder and from finely divided starting powders of the corresponding refractory compounds. When sintering articles of zirconium carbide we used activating additions with which the spheroidized powders were clad, or else the activator was added to the charge. The compacts of niobium carbide and also of refractory compounds having a melting point below 3200°C were generally sintered without the addition of activating substances at a temperature of 0.7 - 0.95 T_f of the corresponding refractory compound.

The starting powders or the spheroidized particles of the refractory compound were mixed with a 5% solution of SK (synthetic rubber) or a 3% solution of polyvinyl alcohol, dried at a temperature of 60 - 80°C, ground through a screen of 1 - 2 mm mesh to break up the lumps, and then pressed. Pressing was done at a pressure from 25×10^5 to 15×10^7 N/m^2 (Newton/m^2). The compacts were dried at 160 - 180°C for 8 - 12 hrs and, if necessary, were machined into the final shape and sintered at appropriate temperatures. As shown by the experiments, the final porosity of the sintered products depends to a great /87 extent on the compaction pressure and on the sintering temperature.

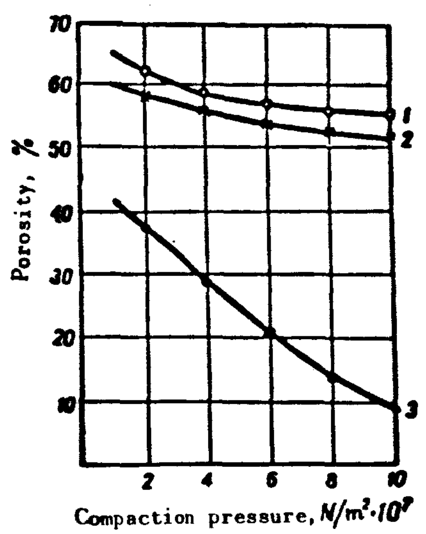

Fig.2 Porosity of the Product as a Function of Compaction Pressure and Sintering Temperature
Sintering temperature: 1 - 1400°C; 2 - 1500°C; 3 - 1600°C

For example, Fig.2 shows the dependence of porosity on the compaction pressure, at various sintering temperatures of the workpiece. The curves were plotted for compacts of chromium carbide (Cr_3C_2) fabricated from spheroidized powders with particle sizes of 100 - 150 μ. As indicated by these curves, the greatest effect of the compaction pressure is observed at the maximal permissible (without fusion of the particles) sintering temperature. Thus, at a compaction pressure of 2×10^7 N/m^2 and a sintering temperature of 1600°C, the porosity of the specimens will be 36%. At the same sintering temperature, but

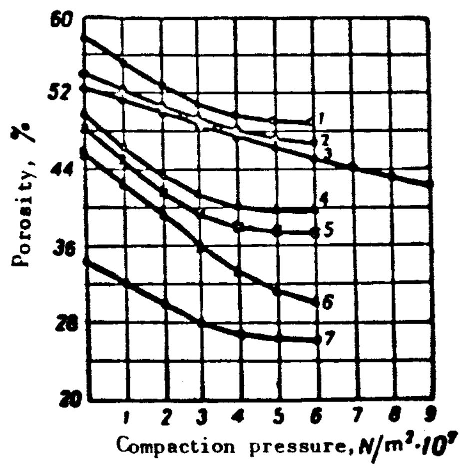

Fig.3 Porosity of Products of Refractory Compounds as a Function of Compaction Pressure
Numbers on curves correspond to compounds shown in the Table

with an increase in compaction pressure, the porosity markedly drops and, at 1×10^8 N/m^2, amounts to only 9%. These specimens have low permeability.

Figure 3 gives a graph for the dependence of the porosity of the sintered products on the compaction pressure, for certain refractory carbides and

Material	No. of Curve in Fig. 3	Particle Size μ	Sintering Temperature °C	Sintering Time, min
Cr_3C_2	1	177—420	1400	60
Cr_3C_2	2	44—75	1400	60
Cr_3C_2	3	3—40	1400	60
$(TiCr)B_2$	4	75—105	2000	30
ZrB_2	5	44—75	2000	30
TiC	6	100—150	2300	60
TiC	7	75—105	2300	60

borides at different grain size of the spheroidized particles. The above Table gives the particle sizes and optimal sintering conditions for porous materials of refractory compounds, yielding maximal porosity at satisfactory strength. /88

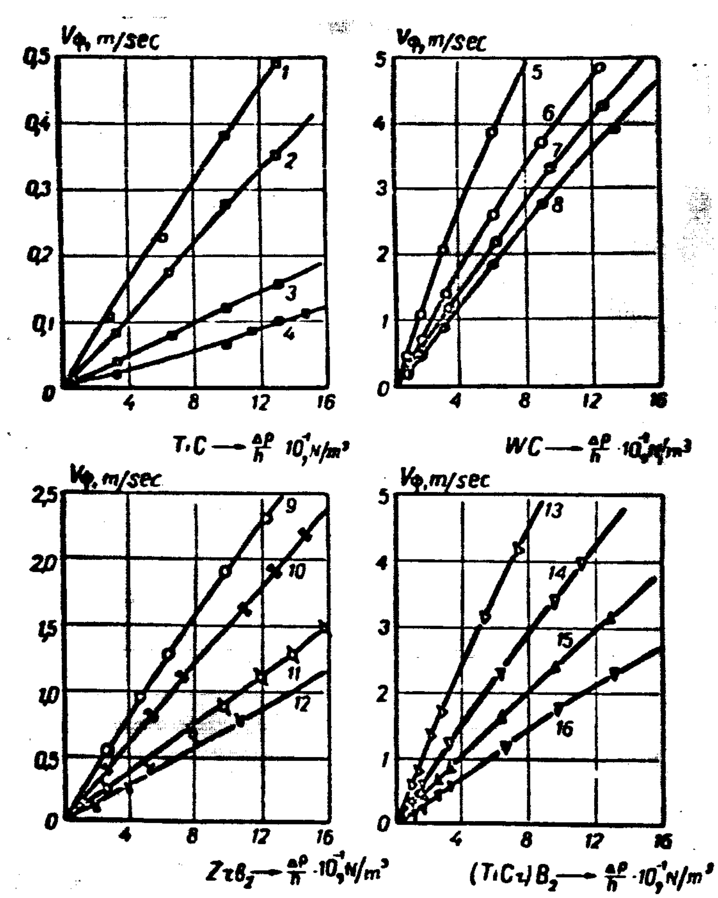

Fig.4 Rate of Nitrogen Filtration as a Function of Pressure Drop and Porosity at 20°C
Porosity (%): 1 - 32.0; 2 - 30.5; 3 - 28.9; 4 - 26.4; 5 - 48.3; 6 - 47.9; 7 - 46.6; 8 - 41.9; 9 - 48.6; 10 - 43.6; 11 - 41.1; 12 - 37.5; 13 - 49.7; 14 - 45.4; 15 - 41.7; 16 - 40.0

It follows from the diagram that, other conditions being equal, the porosity of the specimens of the refractory compounds increases with increase in particle size of the spheroidized powders. Furthermore, the porosity of sintered specimens depends greatly on the material being sintered. Thus, chromium carbide yields specimens with a porosity up to 58% and of satisfactory strength, whereas titanium carbide specimens are obtained with a lower porosity at still satisfactory strength.

Figure 4 gives the rate of nitrogen filtration through porous objects produced from certain refractory compounds, as a function of the pressure drop, referred to unit thickness of the specimen. The curves are given for various porosities of the products. The dependence of the permeability of porous objects made from refractory compounds on the thickness or on the various pressure drops is plotted in Fig.5 which shows that the thickness of the specimen has a considerable influence on its permeability, especially at large pressure drops.

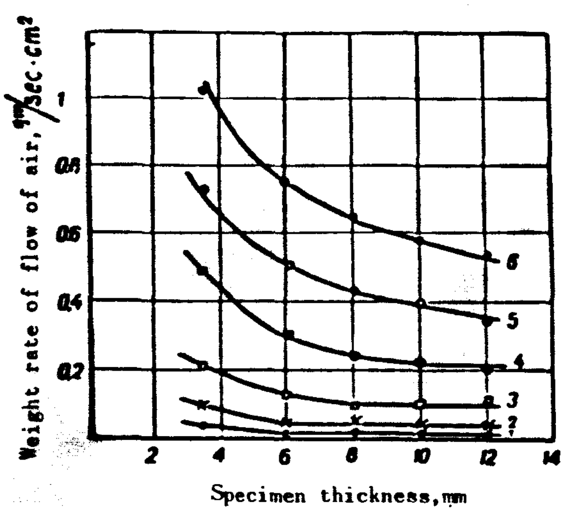

Fig.5 Effect of Thickness of the Objects on their Permeability
Pressure drop (N/cm^2): 1 - 1; 2 - 5; 3 - 10; 4 - 20; 5 - 30; 6 - 40

Permeability measurements have established that this depends largely on /89 the temperature and abruptly decreases with increasing temperature. As an example, Fig.6 gives the change in permeability of a specimen of tungsten carbide as a function of the temperature. It follows from the diagram that, with an increase in operating temperature of the porous tungsten carbide specimen from room temperature to 1100°C, its permeability drops almost tenfold. Since,

at temperatures up to 1100°C, no changes are observed in the character of the /90
specimen porosity, the noted drop in permeability can be explained by an increase in gas viscosity with increasing operating temperature and by the resultant increase in resistance of the specimen to the passage of gas.

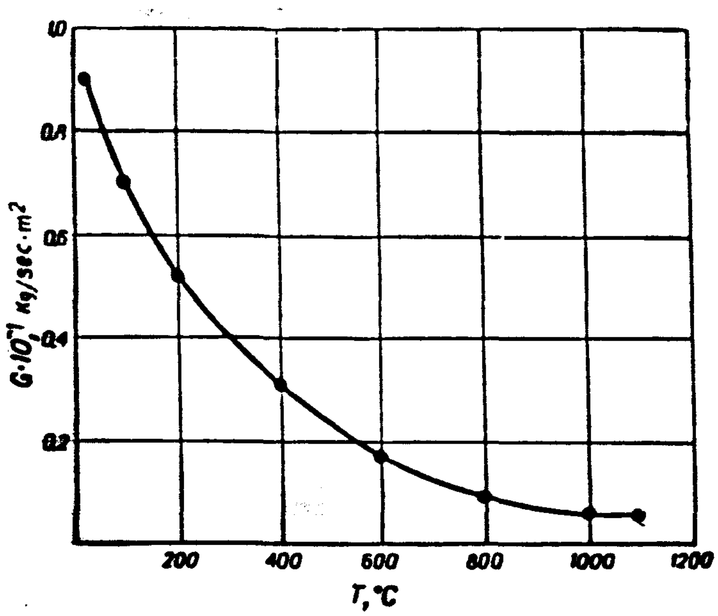

Fig.6 Permeability of Porous Objects of Tungsten Carbide as a Function of Temperature
Blowing with nitrogen. Pressure drop ΔP = 29.4 N/cm^2; specimen thickness δ = 0.33 cm; porosity 47.9%

On the basis of these investigations on the gas permeability of porous specimens of carbides and borides of refractory metals at room temperatures, we defined the viscosity (α) and inertial (β) coefficients by the following formula (Bibl.5, 6) which establishes the relation between the weight rate of flow of the gas and the pressure drop:

$$\frac{P_1^2 - P_2^2}{2hzRT} = \alpha\mu G + \beta G^2,$$

where G is the mass rate of flow of the gas, in kg/sec • m^2; R is the gas constant, in J/kg $\cdot$ ^{o}K; T is the absolute gas temperature, in ^{o}K; μ is the coefficient of dynamic viscosity, in N $\cdot$ sec/m^2; h is the specimen thickness, in m; z is the coefficient of compressibility of the gas.

We found that $\alpha = 8.9 \times 10^{23} P^{-7}$ and $\beta = 6.8 \times 10^{22} P^{-10}$, where P is the porosity of the material, in %. The obtained dependencies for α and β can serve as a first approximation in calculating the hydraulic resistance of objects made of porous carbides and borides.

Conclusions

As a result of these investigations, methods were worked out for fabricating porous materials of carbides and borides of refractory metals by sintering freely poured spheroidized powders and by sintering pre-pressed compacts. The conditions for obtaining objects with a prescribed porosity and permeability were established. The permeability of porous materials of carbides and borides of refractory metals was studied.

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